

General Method for Symmetry Orbitals and Tensors in Electronic Structure Calculations

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ABSTRACT: The symmetry orbital tensor (SOT) method, which makes full use of symmetries in all point groups and can be applied to the self-consistent field (SCF) and post-SCF calculations, is introduced. The principal feature of this method is the definition of the symmetry orbitals (SOs). Any element in a molecular point group will transform one SO to another equivalent SO or simply to itself, and no mixture among SOs exists. Thus, although the SOs for non-Abelian point groups may adapt to reducible representations, their transformation properties are much simpler than in conventional treatments. This article also presents a general scheme to generate SOs for all point groups. The direct products of N SOs form an N th-rank SOT group, and each matrix element between SOTs is the product of a physical factor and a geometric factor. Compared with the canonical molecular orbitals, the use of SOs can noticeably reduce the computation efforts by decreasing the number of integrals needed in the SCF calculations or the number of configurations needed in the configuration interaction (CI) calculations. The SOT-SCF and SOT-CI approaches are formulated and a preliminary SOT-SCF program is written. Pilot calculations demonstrate the value of the SOT approach, at least at the closed-shell Hartree–Fock level. © 1999 John Wiley & Sons, Inc. *J Comput Chem* 20: 305–321, 1999

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Introduction

Although nowadays *ab initio* calculations can be successfully applied to modest-sized molecules, two challenges still linger. One is the nonempirical treatment of biological molecules, such as proteins and nucleic acids. The other is the accurate evaluation of electronic correlation energies. It is clear that the solution to the above challenges heavily depends on computation technologies. However, from the physical point of view, both challenges can be summarized into one pivotal problem: how to reduce the computation efforts to a maximum extent; in other words, how to exploit molecular symmetries in the most efficient way.

The use of symmetry in self-consistent field (SCF) calculations was initiated by Dacre,¹ Edler,² and Dupuis and King.³ Among the point group theories, the irreducible tensor method has been extensively studied and applied.^{4,5} It has become a standard way to construct molecular orbitals (MOs) with the symmetry-adapted linear combinations (SALCs) of primitive atomic orbitals (AOs). The construction of SALCs usually results in a set of canonical MOs (CMOs), which are irreducible bases of molecular point groups. Based on the Wigner–Eckart theorem and the irreducible tensor method, Gershgorin and Shavitt,⁶ Rettrup et al.,⁷ Gao et al.,⁸ and Lam et al. discussed the configuration bases that adapt to space and spin symmetries. However, it is recognized that non-Abelian point group symmetries are very difficult to exploit in post-SCF methods. To overcome this difficulty, Carsky et al.¹⁰ Lazzaretti et al.¹¹ extended the petite list (the list of unique primitive integrals after considering molecular symmetry) approach to post-SCF steps, while Hollauer and Dupuis¹² proposed a very general scheme to obtain molecular integrals from the petite list through the use of Clebsch–Gordan coefficients. Hollauer and Dupuis formalism works for Abelian and non-Abelian point groups. At the configuration interaction (CI) level, Liu and Yoshimine¹³ developed the symbolic matrix method, which can also take full advantage of any point group symmetry in principle. Nevertheless, the practical implementation for non-Abelian groups beyond the SCF approach is by no means trivial. The widely used quantum mechanical softwares like GAUSSIAN 94¹⁴ and GAMESS¹⁵

are still unable to make full use of point group symmetries of non-Abelian groups at the correlated levels, although Abelian point groups have been effectively applied in the full CI algorithm.¹⁶ We believe that the crucial reasons is the use of CMOs or SALCs of AOs as 1-electron basis functions. For point groups with degenerate irreducible representations, symmetry operations may map an AO (or an MO) into a linear combination of k AOs (or MOs) rather than only one single term; consequently, the calculation of N th-rank tensors is a k^N problem and the exploitation of space symmetry adaptation is very difficult when N increases.

In recent years we have been developing a new method for point group symmetry adaptation,¹⁷ which is significantly different from conventional irreducible tensor methods. The key element of our method is the proposal of symmetry orbitals (SOs). The operation of any element of a point group will transform an SO into another SO or simply itself. Thus, although SOs for non-Abelian groups may be reducible, their transformation properties are much simpler than those of CMOs and eventually the use of SOs can remarkably simplify both the SCF and post-SCF calculations. In this article we derive the formulations, which are crucial in the SCF and post-SCF methods, and present some pilot SCF calculation results. We describe the concept of the SO and a general scheme to construct SOs for various point groups. The evaluation of the matrix elements of SO tensors (SOTs) is presented. The simplification of the traditional SCF calculations using our SOs is discussed and demonstrated, while an algorithm for the CI method based on SOs is derived. Finally, some discussions are given.

BASIC CONCEPTS

For a molecule whose point group is $G = \{g\}$ of order K_G , we define a complete space that is composed of a set of orbitals $\{M\}$. We call $\{M\}$ SOs if the operation of any group element g on any orbital will result in another orbital in the same complete space or simply itself. In other words,

$$gM = \zeta M', \quad (1)$$

where ζ is the phase factor. The orbitals $\{M\}$ may be AOs or MOs and generally they are complex. It is clear that the SOs are very different from the traditional CMOs, on which almost all *ab initio* MO methods are based. For a N th-rank SOT

$M(N)$, there is

$$gM(N) = \zeta M'(N), \quad (2)$$

where $M'(N)$ is either equivalent to or identical to $M(N)$. Because the SOs and the SOTs have the same transformation properties, the SOs can generate the SOT representations under G . In the present SOT theory, the formation of SOs and the relation between the SO basis and the CMO basis are two fundamental problems. If real basis functions are used, 1- or 3-dimensional irreducible representations can generate SOs alone; however, 2-dimensional representations are unable to generate SOs alone for the point groups containing a $(2n + 1)$ -fold symmetry axis. Although SOs can be finally generated by the hybridization of 1- and 2-dimensional irreducible basis functions for the point groups having a three-fold axis, it is impossible to obtain SOs for the groups (e.g., C_5 , C_7 , K , I , and linear groups) having a five- or sevenfold axis. For the sake of generality, we did not require that SOs be real. We propose a general scheme to construct SOs for noncentral atoms, a central atom in a finite point group, and linear molecules.

SOs OF NONCENTRAL ATOMS

In most molecular calculations a standard Cartesian coordinate is defined by setting the molecular center of mass as the origin. In the present work, however, we adopt local coordinate systems for all noncenter (ligand) atoms. Suppose (ϕ, θ) represent the angle vectors of atom \mathbf{a} and $e(1, \mathbf{a})$, $e(2, \mathbf{a})$, $e(3, \mathbf{a})$ are the unit vectors in the x , y , z directions of the local coordinate system for atom \mathbf{a} while the three unit vectors of the standard coordinate system in the x , y , z directions are labeled as $e(1)$, $e(2)$, $e(3)$. There are

$$e(1, \mathbf{a}) = e(1)\cos\phi\cos\theta + e(2)\sin\phi\cos\theta - e(3)\sin\theta, \quad (3)$$

$$e(2, \mathbf{a}) = -e(1)\sin\phi + e(2)\cos\phi, \quad (4)$$

$$e(3, \mathbf{a}) = e(1)\cos\phi\sin\theta + e(2)\sin\phi\sin\theta + e(3)\cos\theta. \quad (5)$$

Under the operation of g , atom \mathbf{a} will be transformed to an equivalent atom \mathbf{a}' or itself. If α is the angle between $e(1, \mathbf{a}')$ and $ge(1, \mathbf{a})$ and I represents a simple rotation ($I = 1$) or an image rotation

($I = -1$), there are

$$ge(1, \mathbf{a}) = e(\mathbf{a}')\cos\alpha + e(2, \mathbf{a}')\sin\alpha, \quad (6)$$

$$ge(2, \mathbf{a}) = -e(1, \mathbf{a}')\sin\alpha + e(2, \mathbf{a}')\cos\alpha \quad (I = 1), \quad (7a)$$

$$ge(2, \mathbf{a}) = e(1, \mathbf{a}')\sin\alpha - e(2, \mathbf{a}')\cos\alpha \quad (I = -1), \quad (7b)$$

$$ge(3, \mathbf{a}) = e(3, \mathbf{a}'). \quad (8)$$

Thus, the operation of g on the unit vectors of local coordinate systems can be characterized by three indexes $(\mathbf{a}, I, \mathbf{a}')$. The rotation angle α satisfies

$$\text{mod}(K_G\alpha, 360^\circ) = 0. \quad (9)$$

For a complex basis function $M(l, m, \mathbf{a})$ and two real basis functions $M(l, m_x, \mathbf{a})$ and $M(l, m_y, \mathbf{a})$ in the local coordinate system of atom \mathbf{a} , there is

$$M(l, m, \mathbf{a}) = 2^{-1/2}(M(l, m_x, \mathbf{a}) + iM(l, m_y, \mathbf{a})). \quad (10)$$

The operation of g on the basis function M can be characterized by two indexes $(M(g), \varphi_g)$, which are derived from

$$\begin{aligned} gM &= gM(l, m, \mathbf{a}) = \exp(m\alpha(g)i)M(l, m', \mathbf{a}') \\ &= \exp(\varphi_g i)M(l, m', \mathbf{a}') \\ &= \exp(\varphi_g i)M(g). \end{aligned} \quad (11)$$

$\{M(g); g \in \mathbf{G}\}$ and $\{\varphi_g; g \in \mathbf{G}\}$ are called the structures of basis functions and phase factors, respectively. $\varphi = m\alpha$ satisfies

$$\text{mod}(K_G\varphi, 360^\circ) = \text{mod}(K_Gm\alpha, 360^\circ) = 0. \quad (12)$$

There are two particular cases for eq. (11), $\varphi = 0$ and $\varphi = 180^\circ$, which will result in $gM = M(g)$ and $gM = -M(g)$, respectively. Now we discuss the transformation of $M(l, m, \mathbf{a})$ in detail, which will eventually generate an SO space. If the number of equivalent atoms with \mathbf{a} is $n - 1$, generally there are the following five cases: (i) $m = 0$. Thus, the quantum number $\varphi = 0$ and

$$gM(l, 0, \mathbf{a}) = M(l, 0, \mathbf{a}'). \quad (13)$$

In other words, $M(l, 0, \mathbf{a})$ spans an n -dimensional SO representation under G . (ii) $m \neq 0$, and for any g the following equation is satisfied:

$$\text{mod}(\varphi_g, 180^\circ) = 0. \quad (14)$$

Thus, $M(l, m_x, \mathbf{a})$ and $M(l, m_y, \mathbf{a})$ span two different representations, and the dimension of each representation is n . (iii) $m \neq 0$, and for any symmetric operator g under G there is

$$\text{mod}(\varphi_g, 90^\circ) = 0; \quad (15)$$

but in the meantime at least one operator is not subject to eq. (14). In this case, $M(l, m_x, \mathbf{a})$ and $M(l, m_y, \mathbf{a})$ are equivalent and can be transformed to each other, but they will not mix under G . Therefore, $M(l, m_x, \mathbf{a})$ and $M(l, m_y, \mathbf{a})$ span two n -dimensional SO representations. (iv) $m \neq 0$, and for one or more operators eq. (15) does not hold; besides, each symmetric operator g satisfying $g\mathbf{a} = \mathbf{a}$ is constrained to be a pure rotation (namely $I = 1$). In this case, the real basis functions $M(l, m_x, \mathbf{a})$ and $M(l, m_y, \mathbf{a})$ can mix with each other under G , but the complex bases $M(l, m, \mathbf{a}) = M(l, -m, \mathbf{a})$ cannot. Therefore, $M(l, m, \mathbf{a})$ and $M(l, -m, \mathbf{a})$ span two n -dimensional SO complex representations, respectively. (v) $m \neq 0$, and at least one operator does not satisfy eq. (15), and one or more operators satisfy $g\mathbf{a} = \mathbf{a}$ and $I = -1$ simultaneously, then $M(l, m, \mathbf{a})$ and $M(l, -m, \mathbf{a})$ can permute each other and span a $2n$ -dimensional SO representation.

SOs OF CENTRAL ATOM

For the central atom, we use the standard coordinate system to construct its SOs with the following two cases of single-axis groups and cubic groups.

Single-Axis Groups (C_n , D_n , C_{nv} , C_{nh} , D_{nd} , S_n)

For a single-axis group the unit vector $e(3)$ along the z axis cannot mix with the xy plane under G . If g is a single rotation C_n or a plane of symmetry through the z axis, there is

$$g(e(3)) = \exp(\alpha i)e(3) = e(3), \quad (16)$$

where the phase angle $\alpha = 0$. If g is C_2 or σ_h in the xy plane or C_i , then

$$g(e(3)) = \exp(\alpha i)e(3) = -e(3), \quad (17)$$

where $\alpha = 180^\circ$. The operation of g on $e(1)$ results in

$$g(e(1)) = e(1)\cos \alpha + e(2)\sin \alpha. \quad (18)$$

If g is a net rotation and $g(e(3)) = e(3)$ or g is an image rotation and $g(e(3)) = -e(3)$, then

$$g(e(2)) = -e(1)\sin \alpha + e(2)\cos \alpha. \quad (19)$$

If g is a net rotation and $g(e(3)) = -e(3)$ or g is an image rotation and $g(e(3)) = e(3)$, then

$$g(e(2)) = e(1)\sin \alpha - e(2)\cos \alpha. \quad (20)$$

The transformation of basis functions on the central atom can be discussed as the following two cases: (i) $m = 0$. If $\text{mod}(l, 2) = 0$, then

$$gM(l, 0) = M(l, 0), \quad (21)$$

which indicates the rotation angle $\alpha = 0$ and as a consequence, basis function $M(l, 0)$ spans a 1-dimensional totally symmetric SO representation. If $\text{mod}(l, 2) = 1$, then the transformation of $M(l, 0)$ and $e(3)$ are the same under G , and $\alpha = 0$ or $\alpha = 180^\circ$. (ii) $m \neq 0$. According to the rotation angle α there are the following situations:

1. For all symmetry operators, eq. (14) holds. Thus, $M(l, m_x)$ and $M(l, m_y)$ cannot mix with each other and span two 1-dimensional SO representations, respectively.
2. For all symmetry operations, eq. (15) holds but eq. (14) is not satisfied by all operations. Consequently, $M(l, m_x)$ and $M(l, m_y)$ can commute to each other but cannot mix under G and they span a 2-dimensional representation.
3. At least one operation does not satisfy eq. (15), and for all symmetry operations $e(2)$ is transformed according to eq. (19); then $M(l, m)$ and $M(l, -m)$ span two 1-dimensional complex representations separately.
4. At least one operation does not satisfy eq. (15), and for at least one operation $e(2)$ is transformed according to eq. (20); then $M(l, m)$ and $M(l, -m)$ can interchange with each other but do not mix under G . $M(l, m)$ and $M(l, -m)$ span a 2-dimensional complex SO representation.

Cubic Groups (O , T , O_h , T_d , T_h)

The basic feature of cubic groups is that the unit vector $e(1)$, $e(2)$, $e(3)$ can interchange to but cannot mix with one another under G . The SO basis functions of the central atom cannot be classified by the magnetic quantum number like in single-axis groups. We deal with the s , p , d , f shells individually as follows: (i) The s shell forms a 1-dimensional totally symmetric SO representation; (ii) $-p_x$, p_y , p_z correspond to $e(1)$, $e(2)$, $e(3)$, respectively, and span a 3-dimensional SO repre-

sensation; (iii) similar to p_x , p_y , and p_z , the d_{yz} , d_{xz} , and d_{xy} span a 3-dimensional SO representation, too. On the other hand, d_{z^2} and $d_{x^2-y^2}$ can mix with each other under G . However, if we define two new complex basis functions

$$\begin{aligned} & \frac{1}{\sqrt{2}}(d_{z^2} + id_{x^2-y^2}) \\ &= \frac{1}{\sqrt{3}} \left(d_{z^2} + \exp\left(\frac{2}{3}\pi i\right)d_{x^2} + \exp\left(\frac{4}{3}\pi i\right)d_{y^2} \right) \end{aligned} \quad (22)$$

and

$$\begin{aligned} & \frac{1}{\sqrt{2}}(d_{z^2} - id_{x^2-y^2}) \\ &= \frac{1}{\sqrt{3}} \left(d_{z^2} + \exp\left(\frac{4}{3}\pi i\right)d_{x^2} + \exp\left(\frac{2}{3}\pi i\right)d_{y^2} \right), \end{aligned} \quad (23)$$

they will not mix with each other under G . Under the operation of C_3 (in the 111 direction), there are

$$C_3(d_{z^2} + id_{x^2-y^2}) = \exp\left(\frac{2}{3}\pi i\right)(d_{z^2} + id_{x^2-y^2}), \quad (24)$$

$$C_3(d_{z^2} - id_{x^2-y^2}) = \exp\left(\frac{4}{3}\pi i\right)(d_{z^2} - id_{x^2-y^2}). \quad (25)$$

For the point group T , $d_{z^2} + id_{x^2-y^2}$ and its conjugate complex basis $d_{z^2} - id_{x^2-y^2}$ form two 1-dimensional representations. However, for T_d , T_h , O_h , and O groups, operators such as σ_d and σ_h may make $d_{z^2} + id_{x^2-y^2}$ and $d_{z^2} - id_{x^2-y^2}$ interchange to each other; thus, these two complex basis functions span a 2-dimensional SO representation. (iv) In the case of the f shell, f_{xyz} spans a 1-dimensional representation while f_{x^3} , f_{y^3} , f_{z^3} and $f_{x(z^2-y^2)}$, $f_{y(z^2-x^2)}$, $f_{z(x^2-y^2)}$ span two 3-dimensional SO representations:

$$f_{x^3} = -\frac{1}{4}[\sqrt{6}f_{xz^2} - \sqrt{10}f_{x(x^2-3y^2)}], \quad (26)$$

$$f_{y^3} = -\frac{1}{4}[\sqrt{6}f_{yz^2} + \sqrt{10}f_{y(3x^2-y^2)}], \quad (27)$$

$$f_{z^3} = f_{z^3}, \quad (28)$$

$$f_{z(x^2-y^2)} = f_{z(x^2-y^2)}, \quad (29)$$

$$f_{x(z^2-y^2)} = \frac{1}{4}[\sqrt{10}f_{xz^2} + \sqrt{6}f_{x(3y^2-z^2)}], \quad (30)$$

$$f_{y(z^2-x^2)} = \frac{1}{4}[\sqrt{10}f_{yz^2} - \sqrt{6}f_{y(3x^2-y^2)}]. \quad (31)$$

Like ligand atoms, the SO representations for the central atom can also be characterized by two indexes: $\{M(g); g \in G\}$ and $\{\varphi_g; g \in G\}$.

SOs IN LINEAR MOLECULES

Linear molecules belong to $C_{\infty v}$ and $D_{\infty h}$ infinite point groups, and the MOs are distinguished according to the magnetic quantum number m . The orbitals with $m = 0, 1, 2, \dots$ are known as σ , π , $\delta \dots$ MOs, respectively. The σ orbitals form 1-dimensional irreducible representations and the π , δ, \dots orbitals generate 2-dimensional representations. For linear groups, only complex bases can satisfy eq. (1) and ζ are complex numbers. We introduce two new finite groups C^* and D^* , which correspond to $C_{\infty v}$ and $D_{\infty h}$ point groups, respectively. The C^* has two elements: one is the identity e and the other is the complex conjugate element $*$. The D^* group has four elements: e , $*$, inversion I , and I^* . The operations C_{∞} and σ in $C_{\infty v}$ and $D_{\infty h}$ are discarded here. The significant advantage of C^* and D^* groups is their simplicity and completeness to classify MOs for all linear molecules. Because $C_{\infty v}$ is the subgroup of $D_{\infty h}$ we only discuss here the D^* group with an example of the AX_2 molecule.

Suppose that the z axis is the quantization axis and atom 1 is located on the positive z axis, atom 2 on the negative z axis, and atom 3 (A in AX_2) at the origin. The AOs are written as $f(\mathbf{a}, l, m)$, where \mathbf{a} is the notation of an atom (in this case \mathbf{a} may be 1, 2, or 3), l is the angular quantum number, and m is the magnetic quantum number. The MOs are written as $F(k, m)$, where $k = 1$ or -1 represents symmetry (g) or antisymmetry (u) under the operation of I . There are

$$*f(\mathbf{a}, l, m) = f(\mathbf{a}, l, -m), \quad (32)$$

$$*F(k, m) = F(k, -m), \quad (33)$$

$$IF(k, m) = kF(k, m), \quad (34)$$

where $f(\mathbf{a}, l, m)$ and $F(k, m)$ (if $m > 0$) are complex functions and each can be expressed as a product of a real function $f_r(\mathbf{a}, l, m)$ or $F_r(k, m)$ and an angular function $\exp(im\varphi)$

$$\begin{aligned} f(\mathbf{a}, l, m) &= f_r(\mathbf{a}, l, m)\exp(im\varphi) \\ &= f_r(\mathbf{a}, l, m)(\cos m\varphi + i\sin m\varphi) \\ &= 2^{-1/2}(f(\mathbf{a}, l, m_x) + if(\mathbf{a}, l, m_y)), \end{aligned} \quad (35)$$

$$\begin{aligned} F(k, m) &= F_r(k, m)\exp(im\varphi) \\ &= F_r(k, m)(\cos m\varphi + i\sin m\varphi), \end{aligned} \quad (36)$$

where $F(k, m)$ are a linear combination of $f(\mathbf{a}, l, m)$. For the present AX_2 system, all possible SMOs can be constructed as follows:

$$\begin{aligned}
 F(1, 0): & \quad f(1, 0, 0) + f(2, 0, 0); f(3, 0, 0); \\
 & \quad f(1, 1, 0) - f(2, 1, 0); \\
 & \quad f(1, 2, 0) + f(2, 2, 0); \\
 & \quad f(3, 2, 0); f(1, 3, 0) - f(2, 3, 0); \\
 F(-1, 0): & \quad f(1, 0, 0) - f(2, 0, 0); \\
 & \quad f(1, 1, 0) + f(2, 1, 0); f(3, 1, 0); \\
 & \quad f(1, 2, 0) - f(2, 2, 0); \\
 & \quad f(1, 3, 0) + f(2, 3, 0); \\
 & \quad f(3, 3, 0); \\
 F(1, 1): & \quad f(1, 1, 1) - f(2, 1, 1); \\
 & \quad f(1, 2, 1) + f(2, 2, 1); \\
 & \quad f(3, 2, 1); f(1, 3, 1) - f(2, 3, 1); \\
 F(1, -1): & \quad f(1, 1, -1) - f(2, 1, -1); \\
 & \quad f(1, 2, -1) + f(2, 2, -1); \\
 & \quad f(3, 2, -1); f(1, 3, -1) - f(2, 3, -1); \\
 F(-1, 1): & \quad f(1, 1, 1) + f(2, 1, 1); \\
 & \quad f(3, 1, 1); f(1, 2, 1) - f(2, 2, 1); \\
 & \quad f(1, 3, 1) + f(2, 3, 1); \\
 & \quad f(3, 3, 1); \\
 F(-1, -1): & \quad f(1, 1, -1) + f(2, 1, -1); \\
 & \quad f(3, 1, -1); f(1, 2, -1) - f(2, 2, -1); \\
 & \quad f(1, 3, -1) - f(2, 3, -1); \\
 & \quad f(3, 3, -1); \\
 F(1, 2): & \quad f(1, 2, 2) + f(2, 2, 2); \\
 & \quad f(3, 2, 2); f(1, 3, 2) - f(2, 3, 2); \\
 F(1, -2): & \quad f(1, 2, -2) + f(2, 2, -2); \\
 & \quad f(3, 2, -2); f(1, 3, -2) - f(2, 3, -2); \\
 F(-1, 2): & \quad f(1, 2, 2) - f(2, 2, 2); \\
 & \quad f(1, 3, 2) + f(2, 3, 2); f(3, 2, 2); \\
 F(-1, -2): & \quad f(1, 2, -2) - f(2, 2, -2); \\
 & \quad f(1, 3, -2) + f(2, 3, -2); f(3, 2, -2); \\
 F(1, 3): & \quad f(1, 3, 3) - f(2, 3, 3); \\
 F(1, -3): & \quad f(1, 3, -3) - f(2, 3, -3); \\
 F-1, 3: & \quad f(1, 3, 3) + f(2, 3, 3); f(3, 3, 3); \\
 F(-1, -3): & \quad f(1, 3, -3) + f(2, 3, -3); \\
 & \quad f(3, 3, -3).
 \end{aligned}$$

Subject to the above relations, all SMOs $\{F(k, m)\}$ composed of s , p , d , and f shells can be divided into 14 classes and eight irreducible representations with respect to the quantum numbers k and m . $F(k, m)$ and $F(k, -m)$ ($m > 0$) are two equivalent components of a 2-dimensional irreducible

representation. Based upon symmetric reasons, we have

$$\langle F(k, m) | F'(k', m') \rangle = \delta(k, k') \delta(m, m') S(F, F'). \quad (37)$$

Thus, the MOs of different blocks with different k and m are orthogonal, while these of the same block with the same k and m can be orthogonalized via a Lowdin or Schmidt scheme. Consequently, a complete set of orthogonal SOs is generated. The SOs of linear molecules are CMOs belonging to C^* and D^* , which are Abelian groups.

In summary, for all point groups and all molecular systems the SOs can be generated and standardized according to different rules as mentioned above. For the finite point groups, the SOs of a noncentral atom \mathbf{a} are irreducible basis functions belonging to the subgroup G_a composed of symmetric operations satisfying $g\mathbf{a} = \mathbf{a}$. When the coset generator g_a of G_a satisfying $g\mathbf{a} = \mathbf{a}'$ acts on the SOs of atom \mathbf{a} , the SOs of \mathbf{a}' are generated. On the other hand, the SOs of the central atom are irreducible basis functions under group G , and there are different generation schemes for the point groups with one main axis and for the cubic groups. For the single-axis groups, the z axis and $e(3)$ does not mix with the xy plane. The basis function $M(l, 0)$ spans a 1-dimensional irreducible representation, while for $m \neq 0$ $M(l, m)$ may span 1- or 2-dimensional real or complex representations based on different cases. For the cubic groups two complex bases $d_{z^2} + id_{x^2-y^2}$ and $d_{z^2} - id_{x^2-y^2}$ can be interchanged but cannot mix with each other under the operation of G . The three basis functions belonging to 3-dimensional representations correspond to $e(1)$, $e(2)$, $e(3)$ individually, but different 3-dimensional representations have different phase factor structures. If two sets of phase factor structures are the same, the two sets of SOs belong to the same representation (e.g., p_x , p_y , p_z and d_{yz} , d_{xz} , d_{xy} in the case of group T). The SOs of the central atom for groups I and K are not considered because generally there is no such case. For linear molecules of $C_{\infty v}$ and $D_{\infty h}$ point groups, two new finite groups C^* and D^* are introduced. The $C_{\infty v}$ and $D_{\infty h}$ are net point groups without considering the time-reversal operator, but in the C^* and D^* groups the time-reverse or the complex conjugate element $*$ is included. The $D_{\infty h}$ group consists of four 1-dimensional irreducible representations (Σ_g^+ , Σ_u^+ , Σ_g^- , and Σ_u^-), while the D^* group consists of only two 1-dimensional irreducible representations. However, no MO belongs

to Σ_g^- and Σ_u^- ; therefore, compared with the traditional $C_{\infty v}$ and $D_{\infty h}$ point groups, the symmetry characterizations of the C^* and D^* groups are more complete and simpler for linear molecules. Besides, the irreducible representations of C^* and D^* groups can be characterized with two quantum numbers (k, m) , which can completely classify MOs. The orbitals represented by (k, m) satisfy eq. (1) and therefore are SOs.

Whether the SOs are real or complex depends on the transformation properties under G . In other words, the SOs are real if eq. (15) is satisfied by all operations and the SOs must be complex if at least one operation of G does not satisfy eq. (15).

SOT Representation and Matrix Element Evaluation

DIRECT PRODUCT REPRESENTATION AND SOT GROUP

All N -rank tensors $M(N) = M_1 M_2 \cdots M_N$ ($N = 1, 2, 3, 4, \dots$) satisfying eq. (2) span SOT representations. To generate a complete set of SOTs we introduce three indexes s , t , and u to classify the SOTs. Each SOT can be written as $M(s, t, u)$, where s denotes an SOT representation, t denotes a component of s , and u denotes the multiplicity of the SOTs with the same s and t . The SOTs with the same s and t but different u are covariant under G . For two SOTs $M(s_1, t_1, u_1)$ and $M(s_2, t_2, u_2)$, there are

$$gM(s_1, t_1, u_1) = \exp(\varphi_1 i) M(s_1, t'_1, u_1), \quad (38)$$

$$gM(s_2, t_2, u_2) = \exp(\varphi_2 i) M(s_2, t'_2, u_2), \quad (39)$$

where s and u in $M(s, t, u)$ are invariant under G . Now we consider the transformation of the direct product of two SOTs under G :

$$\begin{aligned} gM(s, t, u) &= g(M(s_1, t_1, u_1)M(s_2, t_2, u_2)) \\ &= \exp(\varphi_1 i) M(s_1, t'_1, u_1) \\ &\quad \times \exp(\varphi_2 i) M(s_2, t'_2, u_2) \\ &= \exp((\varphi_1 + \varphi_2) i) M(s, t', u). \end{aligned} \quad (40)$$

Therefore, the direct product of two SOTs is still a SOT. Moreover, the phase factors are additive, namely, $\varphi = \varphi_1 + \varphi_2$ and

$$M(s_1, t_1, u_1)M(s_2, t_2, u_2) = M(s, t, u). \quad (41)$$

$M(s_1, t_1, u_1)$ and $M(s_2, t_2, u_2)$ are permutable under G except for the case of $s_1 = s_2$ and $u_1 \neq u_2$, $t_1 \neq t_2$.

Among SOTs, $M(s, t, u)$ with $t = 1$ is called the character tensor (CT). Because all $M(s, t, u)$ with different t and the same s and u are equivalent and can be transformed to one another, each SOT representation can be characterized by a CT. Based on eqs. (1) and (2), we can construct a subgroup $G_a = \{g_a\}$ of order K_a . For each element g_a there is

$$g_a M(s, 1, u) = \exp(\varphi_a i) M(s, 1, u). \quad (42)$$

In total there are K_a phase factors corresponding to G_a , which form the phase factor structure $\{\varphi_a\}$ of $M(s, 1, u)$. It is obvious that $M(s, 1, u)$ is the eigenfunction of an operator g_a of the subgroup G_a and $\exp(\varphi_a i)$ is the eigenvalue. Let g_t be a coset generator of G_a ; there is

$$g_t M(s, 1, u) = \exp(\varphi_t i) M(s, t, u) \quad t = 2, \dots, K_s, \quad (43)$$

where $K_s = K_G/K_a$ and $\{M(s, t, u), t = 1, 2, \dots, K_s\}$ span a K_s -dimensional SOT representation. For a given point group, the number of subgroups is limited and definite. In the meanwhile, for a given subgroup, its phase factor structures, which must satisfy eq. (12), is also limited and definite. Consequently, for each point group, there is a set of SOT representations whose number is very limited. Each SOT representation is characterized by a subgroup $\{g_a\}$ whose phase factor structure corresponds to $M(s, 1, u)$. Because the direct product of two SOTs is still a SOT, the multiplication operation of SOT is closed and SOTs form a finite SOT group. From the group multiplication table of a SOT group, the representation of the direct product of two SOTs can be easily generated. Finally, it should be noted that the N th-rank tensor generated by an N -fold product of SOs is a SOT rather than a combination of several terms.

MATRIX ELEMENTS BETWEEN SOs

The evaluation of the matrix elements between SOTs is the core in our SOT method. In the irreducible representation tensor method, the most important feature is the complete separation of matrix elements into physical factors and geometric factors and only the matrix elements belonging to the totally symmetric irreducible representation are nonzero. In the present SOT method, the matrix element of a totally symmetric operator between $M(s_1, t_1, u_1)$ and $M(s_2, t_2, u_2)$, which is denoted as $\underline{M}(s_3, t_3, u_3)$, is of the same transformation properties as the SOT $M^*(s_1, t_1, u_1)$

$M(s_2, t_2, u_2) = M(s_3, t_3, u_3)$. At first we consider the CT $M(s, 1, u)$ for $\{M(s, t, u), t = 1, 2, \dots, K_s\}$. If the matrix element $\underline{M}(s, l, u)$ corresponding to $M(s, 1, u)$ is nonzero, from eq. (42) there is

$$\exp(\varphi_a i) = 1, \quad \varphi_a = 0 \quad \{a = 1, \dots, K_a\}, \quad (44)$$

and from eq. (43) we can derive

$$\underline{M}(s, t, u) = \exp(-\varphi_t i) \underline{M}(s, 1, u). \quad (45)$$

Equation (45) indicates that $\{\underline{M}(s, t, u)\}$ with the same s and u but different t are different in the phase factor and are nonzero only if $\underline{M}(s, 1, u)$ is nonzero. The nonzero $\underline{M}(s, 1, u)$ can be defined as the physical factors and the phase factors may be renamed as the geometric factors. Therefore, like the irreducible representation tensor method, in the SOT method the matrix elements between SOs are also the products of physical factors and geometric factors.

The SOT method and the irreducible representation tensor method are completely equivalent, because both realize the full separation of physical factors and geometric factors. The difference between these two methods lies in the fact that each physical factor is composed of only one term in the SOT method, but in the irreducible representation tensor method a physical factor may consist of several terms whose number increases with N . Moreover, in the irreducible representation tensor method various coupling coefficients are necessary and different point groups need different coupling coefficients. In general, compared with the irreducible representation tensor method, the SOT method greatly reduces the computation efforts in the order of $k^N \rightarrow I^N \rightarrow 1$.

$M(s, t, u)$ and its complex conjugate tensor $M^*(s, t, u)$ have the same basis function structures $\{M(g); g \in G\}$, but the phase factor structure for the latter is $\varphi_g(M^*) = 360^\circ - \varphi_g(M)$. Whether the corresponding matrix element $\underline{M}(s, t, u)$ is real or complex depends on the phase factor structure and there are three cases: (i) if $\text{mod}(\varphi_g, 180^\circ) = 0$ for all g , then $\underline{M}(s, t, u)$ must be real and $M(s, t, u)$ may be classified as the first class SOT; (ii) $M^*(s, t, u) \neq M(s, t, u)$ but they belong to the same SOT representation. We assume $M^*(s, 1, u) = M(s, t, u)$. Because any symmetric operation will not alter a matrix element, from eq. (43) there is

$$g_t \underline{M}(s, 1, u) = \underline{M}(s, 1, u) = \exp(\varphi_t i) \underline{M}^*(s, 1, u). \quad (46)$$

If we set $M'(s, 1, u) = \exp(-\varphi_t i/2) M(s, 1, u)$, then the corresponding matrix element $\underline{M}'(s, 1, u)$ must be real. $M(s, t, u)$ in this case is classified as the second class SOT. (iii) $M^*(s, t, u)$ and $M(s, t, u)$ belong to different SOT representations and we classify $M(s, t, u)$ as the third SOT. In this case the computational cost and the storage requirement are about 2 times more than the case of (i) and (ii). This kind of situation is fairly rare for most point groups.

We rewrite eq. (43) as

$$g_t M(s, 1, u) = \exp(\varphi_t i) M(s, t, u) = M''(s, t, u). \quad (47)$$

Because $\underline{M}''(s, t, u)$ is invariable with respect to t ($t = 1, 2, \dots, K_s$), we define

$$\underline{M}_s = \frac{K_s}{K_G} \sum_{g \in G} g \underline{M}''(s, 1, u) = K_s M''(s, 1, u), \quad (48)$$

and \underline{M}_s is called the group matrix element.

IRREDUCIBLE REPRESENTATION GROUP-SYMMETRIC FUNCTIONS

The projection operator for an irreducible representation in a point group is

$$P_{\mu\nu}^{[\lambda]} = \frac{d_\lambda}{K_G} D_{\mu\nu}^{[\lambda]}(g)^* g, \quad (49)$$

where d_λ is the dimension of the irreducible representation λ and μ and ν are the components of λ . We define a full projection operator $P^{[\lambda]}$ as

$$P^{[\lambda]} = \frac{1}{d_\lambda} \sum_{\mu, \nu} P_{\mu\nu}^{[\lambda]} = \frac{1}{K_G} \sum_{\mu, \nu, g} D_{\mu\nu}^{[\lambda]}(g)^* g. \quad (50)$$

The operation of the above operator on a CT $M(s, 1, u)$ will deduce the component of λ symmetry from the CT

$$P^{[\lambda]} M(s, 1, u) = M_\lambda(s, 1, u), \quad (51)$$

and $M_\lambda(s, 1, u)$ has the following properties:

$$\begin{aligned} \text{(i)} \quad M_\lambda(s, 1, u) &= \sum_t \varepsilon(s, t, \lambda) M(s, t, u) \\ &= \sum_\nu \varepsilon(\lambda, \nu) \chi_\nu^{[\lambda]}, \end{aligned} \quad (52)$$

where $\varepsilon(s, t, \lambda)$ and $\varepsilon(\lambda, \nu)$ are coefficients and $\chi_\nu^{[\lambda]}$ is the ν th basis of λ symmetry;

$$\begin{aligned} \text{(ii)} \quad gM_\lambda(s, 1, u) &= \sum_t \varepsilon(s, t, \lambda, g) M(s, t, u) \\ &= \sum_\nu \varepsilon(\lambda, \nu, g) \chi_\nu^{[\lambda]}; \end{aligned} \quad (53)$$

$$\begin{aligned} \text{(iii)} \quad gM_\lambda^*(s, 1, u) M_\lambda(s, 1, u) \\ = M_\lambda^*(s, 1, u) M_\lambda(s, 1, u). \end{aligned} \quad (54)$$

The above formula indicates that density functions are invariant under the symmetric operations.

$$\begin{aligned} \text{(iv)} \quad \langle M_\lambda(s, 1, u) | M_\lambda(s, 1, u) \rangle \\ = \sum_\nu \langle \chi_\nu^{[\lambda]} | \chi_\nu^{[\lambda]} \rangle \varepsilon(\lambda, \nu)^* \varepsilon(\lambda, \nu) \\ = \sum_\nu \varepsilon(\lambda, \nu)^* \varepsilon(\lambda, \nu) = \varepsilon(\lambda) dx \end{aligned} \quad (55)$$

where $\varepsilon(\lambda) = \varepsilon(\lambda, \nu)^* \varepsilon(\lambda, \nu)$ is a positive real number independent on ν .

(v) If $M(s, 1, u)$ belongs to the first or second class representation, $M_\lambda(s, 1, u)$ is real. If $M(s, 1, u)$ belongs to the third class representation, we define

$$M'_\lambda(s, 1, u) = (M_\lambda(s, 1, u) + M_\lambda^*(s, 1, u))/2. \quad (56)$$

Then in any case, $M'_\lambda(s, 1, u)$ is real.

There are three important totally symmetric operators (identity and the 1-electron and 2-electron operators) in quantum chemistry that can be uniformly labeled as A . The matrix element between two irreducible representation functions is

$$\begin{aligned} \langle M_\lambda(s, 1, u) | A | M_\lambda(s', 1, u') \rangle \\ = \sum_{t, t'} \varepsilon^*(s, t, \lambda) \varepsilon(s', t', \lambda) \\ \times \langle M(s, t, u) | A | M(s', t', u') \rangle \\ = \sum_{k, t_k} \underline{M}(s_k, t_k, u_k) \varepsilon(\lambda, k) \\ = \sum_k d_{s_k} \underline{M}(s_k, 1, u_k) \varepsilon(\lambda, k) \\ = \sum_k \underline{M}(k) \varepsilon(\lambda, k). \end{aligned} \quad (57)$$

Due to the Hermiticity of the above matrix element, only the real part (the physical factor) of the matrix element contributes to the final results and the virtual part (the geometric factor) will be cancelled out. If the real and virtual parts of $M(k)$ are

$M_R(k)$ and $M_V(k)$, respectively, there is

$$\langle M_{\lambda R}(s, 1, u) | A | M_{\lambda R}(s', 1, u') \rangle = \sum_k \underline{M}_R(k, \lambda). \quad (58)$$

Equations (57) and (58) are especially useful in the CI methods, as will be shown in a later section.

SOT-SCF Approach

For a given molecular system with n MOs, there are in total $n_2 = (n + 1)n/2$ 1-electron integrals (or overlap integrals) and $n_4 = (n_2 + 1)n_2/2$ 2-electron integrals if only the symmetry of indexes is taken into account. However, when the point group symmetries are introduced, we can find that not all the variable parameters are independent and there are redundant variants. We take CH_4 as an example to describe this point. CH_4 belongs to the point group of T_d and the four hydrogen atoms are symmetric and equivalent; so are the tensors constructed from the atom-atom direct products. Table I lists the atoms and the corresponding two-order tensors (edges) and four-order tensors (tetrahedrons) classified by the equivalence. From Table I we can see that in CH_4 there are two basic atoms, four basic edges, and 17 basic tetrahedrons. Any 1-electron integral or overlap integral must correspond to an edge, while any 2-electron integral must correspond to a tetrahedron. We call the 1-electron integrals corresponding to the basic edges as unique 1-electron integrals and the 2-electron integrals corresponding to the basic tetrahedrons as unique 2-electron integrals. From the principle of equivalence it is clear that the integral terms of the equivalent edges or the equivalent tetrahedrons have the same contribution to matrix elements. As the first simplification rule, nonunique integrals are redundant parameters. With the SOT theory, the number of variable parameters can be reduced further. Table II lists all SOs of different representations for CH_4 (with the 6-311G** basis set), and Table III list the dimension and the multiplicity of each representation. From Table II we can learn that in the model system of CH_4 with the 6-311G** basis set there are five representations and 14 character orbitals. Because 1-electron integrals, overlap integrals [SOT(2)s], and 2-electron integrals [SOT(4)s] can be constructed from the dual and the quarter direct products of SOs, respectively, they can also be characterized and classified by the indexes s , t , and u . Table IV presents the numbers (N_2 and N_4)

TABLE I.
Atoms and Second-Order Tensors (Edges) and Fourth-Order Tensors (Tetrahedrons) Classified by Equivalence for CH₄ of T_d Symmetry.

Rank	Dimension	Basic Atom Tensor ^a		Nonbasic Atom Tensor ^a										
1	4	1	2 3 4											
1	1	5												
2	4	1-1	2-2 3-3 4-4											
2	6	1-2	1-3 1-4 2-3 2-4 3-4											
2	4	1-5	2-5 3-5 4-5											
2	1	5-5												
4	4	1111	2222 3333 4444											
4	12	1112	1113 1114 2221 2223 2224 3331 3332 3334 4441 4442 4443											
4	6	1212	1313 1414 2323 2424 3434											
4	6	1122	1133 1144 2233 2244 3344											
4	12	1213	1214 1314 2123 2124 2324 3132 3134 3234 4142 4143 4243											
4	12	1123	1124 1134 2213 2214 2234 3312 3314 3324 4412 4413 4423											
4	3	1234	1324 1423											
4	4	1115	2225 3335 4445											
4	6	1215	1315 1415 2325 2425 3435											
4	6	1125	1135 1145 2235 2245 3345											
4	4	1235	1245 1345 2345											
4	4	1515	2525 3535 4545											
4	6	1525	1535 1545 2535 2545 3545											
4	4	1155	2255 3355 4455											
4	6	1255	1355 1455 2355 2455 3455											
4	4	1555	2555 3555 4555											
4	1	5555												

^aThe number 1-4 refer to hydrogen atoms and 5 refers to the carbon atom.

of the physical factors (character tensors) of SOT(2)s and SOT(4)s for some typical molecules. For comparison the numbers (n_2 and n_4) of 1-electron and 2-electron integrals without considering molecular symmetries are also listed.

The generation scheme of SOT(2)s and SOT(4)s is generate primitive integrals using routine quantum chemistry software like Gaussian 94.¹⁴ In the SOT method, only the unique integrals corresponding to the basic edges and tetrahedrons

TABLE II.
SO Representations for CH₄(6-311G).**

s	t	u	Atom ^a	Orbital	s	t	u	Atom ^a	Orbital	s	t	u	Atom ^a	Orbital
1	1	1	5	1s	1	1	2	5	2s	1	1	3	5	3s
1	1	4	5	4s	2	1	1	5	2p _x	2	2	1	5	2p _y
2	3	1	5	2p _z	2	1	2	5	3p _x	2	2	2	5	3p _y
2	3	2	5	3p _z	2	1	3	5	4p _x	2	2	3	5	4p _y
2	3	3	5	4p _z	2	1	4	5	3d _{yz}	2	2	4	5	3d _{xz}
2	3	4	5	3d _{yz}	3	1	1	5	3d _{z²} + id _{x²-y²}	3	1	2	5	3d _{z²} - id _{x²-y²}
4	1	1	1	1s	4	2	1	2	1s	4	3	1	3	1s
4	4	1	4	1s	4	1	2	1	2s	4	2	2	2	2s
4	3	2	3	2s	4	4	2	4	2s	4	1	3	1	3s
4	2	3	2	3s	4	3	3	3	3s	4	4	3	4	3s
4	1	4	1	2p _z	4	2	4	2	2p _z	4	3	4	3	2p _z
4	4	4	4	2p _z	5	1	1	1	2p _x + i2p _y	5	2	1	2	2p _x + i2p _y
5	3	1	3	2p _x + i2p _y	5	4	1	4	2p _x + i2p _y	5	5	1	1	2p _x - i2p _y
5	6	1	2	2p _x - i2p _y	5	7	1	3	2p _x - i2p _y	5	8	1	4	2p _x - i2p _y

^aThe numbers 1-4 refer to hydrogen atoms and 5 refers to the carbon atom.

TABLE III.
Dimensions and Multiplicities of SO Representations for CH₄(6–311G**).

S	<i>t_m</i>	<i>u_m</i>	s	<i>t_m</i>	<i>u_m</i>	s	<i>t_m</i>	<i>u_m</i>	s	<i>t_m</i>	<i>u_m</i>	s	<i>t_m</i>	<i>u_m</i>
1	1	4	2	3	4	3	2	1	4	4	4	5	8	1

should be generated and the other integrals are unnecessary. Transform the unique integrals to the SO integrals. Because the transformation from the AOs in the standard coordinate system to the SOs for each shell of an atom is unitary, the transformation from the unique integrals to the SO integrals is simple and fast. The SOT method is a thorough and simple symmetrization method that realizes the separation of physical factors and geometric factors from variable parameters. The ratio between the number of the standard atomic integrals and the number of SO integrals is roughly the order of a point group. Suppose that the order of a point group is *K_G*, there are *n₂/N₂ ≈ K_G* and *n₄/N₄ ≈ K_G*. By using the SO integrals, the disk and memory requirement for the storage of integrals is greatly reduced.

In the SCF iterations the most crucial and time-consuming step is the evaluation of the Fock matrix

$$F_{\mu\nu} = H_{\mu\nu} + G_{\mu\nu}, \tag{59}$$

where

$$G_{\mu\nu} = \sum_{\lambda\sigma} [2(\mu\nu/\lambda\sigma) - (\mu\sigma/\lambda\nu)] D_{\lambda\sigma}. \tag{60}$$

Let

$$[\mu\nu/\lambda\sigma] = 2(\mu\nu/\lambda\sigma) - (\mu\sigma/\lambda\nu), \tag{61}$$

then

$$G_{\mu\nu} = \sum_{\lambda\sigma} [\mu\nu/\lambda\sigma] D_{\lambda\sigma}. \tag{62}$$

Because the number of multiplication operations in an iteration is directly proportional to the number of 2-electron integrals, it is also directly proportional to the fourth power of the number of basis functions. In the equivalent state of a stable molecule, the Hamiltonian and Fock matrices have the same symmetric properties as the frame structure and belong to the totally symmetric irreducible representation of the molecular point group. When SOs are used as 1-electron orbitals, the overlap matrix element *S_{μν}*, the Hamiltonian matrix element *H_{μν}*, *G_{μν} = F_{μν} - H_{μν}*, and the density matrix element *D_{μν}* are SOT(2)s. According to the multiplication rule of direct product representations, these SOT(2)s can also be labeled by the three indexes *s*, *t*, and *u*, namely,

$$X_{\mu\nu} = X(s, t, u) = X(s, 1, u) \exp(-\varphi_t i) \\ (X = S, F, G, H, D), \tag{63}$$

TABLE IV.
Numbers of SOT(2)s and SOT(4)s (*n₂* and *n₄*) and Corresponding Physical Factors (Character Tensors) (*N₂* and *N₄*).

Model	G	Basis	Orbital	<i>n₂</i>	<i>N₂</i>	<i>n₄</i>	<i>N₄</i>
CH ₄	<i>T_d</i>	6–311G**	42	903	85	408156	24074
CH ₆ ²⁺	<i>O_h</i>	6–311G**	54	1485	92	1103355	32659
CH ₆ ²⁻	<i>O_h</i>	6–311G**	54	1485	92	1103355	32659
CH ₈ ⁴⁺	<i>O_h</i>	6–311G**	68	2346	109	2445366	67373
H ₂ O	<i>C_{2v}</i>	6–311G**	30	465	181	108345	35078
C ₅ H ₅ ⁻	<i>C₅</i>	6–311G	55	1540	308	1186570	237314
HF	<i>C_{∞v}</i>	6–311G (<i>df, pd</i>)	36	666	140	222111	26644
N ₂	<i>D_{∞h}</i>	6–311G**	36	666	94	222111	20439
H ₆	<i>D_{6h}</i>	6–311G**	36	666	56	222111	13901
H ₂	<i>D_{∞h}</i>	6–311G (<i>df, pd</i>)	22	561	82	157641	11169
H ₁₂	<i>D_{6h}</i>	6–31G	32	300	24	45140	2531
H ₁₂	<i>I</i>	6–311G	36	666	24	222111	3585

where the parameters $X(s, 1, u)$ are physical factors and the number of each set of parameters is N_2 . Moreover, the SOT(2)s have the same structure of phase factors $\{\varphi_i\}$. The summation term of 2-electron integrals can be rewritten as

$$[\mu\nu/\lambda\sigma] = [stu/s't'u'], \tag{64}$$

and eq. (62) can be rewritten as

$$\begin{aligned} G_{\mu\nu} &= G(s, t, u) = G(s, 1, u)\exp(-\varphi_i i) \\ &= \exp(-\varphi_i i) \sum_{s't'u'} [s1u/s't'u'] D(s', t', u'), \end{aligned} \tag{65}$$

$$\begin{aligned} G(s, 1, u) &= \sum_{s't'u'} [s1u/s't'u'] D(s', t', u') \\ &= \sum_{s't'u'} [s1u/s't'u'] D(s', 1, u') \exp(-\varphi_i i). \end{aligned} \tag{66}$$

Let

$$\{su/s'u'\} = \sum_{t'} [s1u/s't'u'] \exp(-\varphi_i i), \tag{67}$$

then

$$G(s, 1, u) = \sum_{s'u'} \{su/s'u'\} D(s', 1, u'). \tag{68}$$

The above equation is a key for the SOT-SCF calculations and $\{su/s'u'\}$ can be called a group invariant of 2-electron integrals, which is a physical factor in the condensation of indexes for a second- and fourth-order tensors and is invariable in the SOT-SCF iterations. The importance of eq.

(68) lies in the fact that the multiplication manipulations between 2-electron integrals and density matrix elements in the traditional SCF methods have been switched to the multiplication manipulations between the group invariants of 2-electron integrals and the physical factors in density matrix elements. The physical factor $D(s, 1, u)$ is a variable in the SCF calculations. The number of the physical factors $\{su/s'u'\}$ is

$$\begin{aligned} N(g, d) &= N_g N_d = N_2 N_2 \\ &\approx (n_2/K_G)^2 \approx n_4/(K_G)^2. \end{aligned} \tag{69}$$

In the SOT-SCF iterations, only $N(g, d)$ group invariants $\{su/s'u'\}$ need to be restored and the number of multiplication operations to obtain $G(s, 1, u)$ in each iteration is also $N(g, d)$. Thus, compared with the traditional SCF method, the disk and memory requirement and the CPU time in the SOT-SCF method both decrease on the order of $(K_G)^2$. Based on the above derivations, we wrote a preliminary SOT-SCF program. Tables V–IX list the number of MOs, n_2 and N_2 , and n_4 and N_4 , as well as the calculation results from our SOT-SCF program for some model systems of various point group symmetries. Results from standard SCF calculations with Gaussian 94 are also presented for comparisons. Several points should be clarified for the data in these tables:

1. For the sake of simplicity, most of the model systems are hydrogen clusters. However, because p and d AOs are included in the basis sets, the results and discussions should be regarded as general.

TABLE V. Comparison of Calculation Results under Condition That Point Group is C_n (Energy Unit, au).

Model	G	Basis	Orbital	n_2	N_2	n_4	$N(g, d)$	SCF Energy	SOT-SCF Energy
H ₂	C _s	6–311G (<i>df, pd</i>)	22	253	132	32131	17424	–0.831259115	–0.831259115
H ₂	C ₂	6–311G (<i>df, pd</i>)	22	253	132	32131	17424	–0.831259115	–0.831259115
H ₃ ⁺	C ₃	6–311G (<i>df, pd</i>)	33	561	187	157641	34969	–0.960351546	–0.960351546
H ₃ ^{3–}	C ₃	6–311G (<i>df, pd</i>)	33	561	187	157641	34969	–0.823959193	–0.823959193
H ₄ ²⁺	C ₄	6–311G**	24	300	78	45150	6084	–0.845979906	–0.845979906
H ₄ ^{2–}	C ₄	6–311G**	24	300	78	45150	608	–1.734286811	–1.734286812
H ₅ ⁺	C ₅	6–311G**	30	465	93	108345	8649	–0.443227971	–0.443227971
H ₅ [–]	C ₅	6–311G**	30	465	93	108345	8649	–2.507401532	–2.507401532
H ₆	C ₆	6–311G**	36	666	114	222111	12996	–3.055434873	–3.055434873
H ₇ ⁺	C ₆	6–311G**	42	903	129	408156	16641	–3.322990456	–3.322990456
H ₇ ^{3–}	C ₆	6–311G**	42	903	129	408156	16641	–2.953519427	–2.953519427
H ₈ ²⁺	C ₈	6–311G**	48	1176	150	692076	22500	–3.287565678	–3.287565783
H ₈ ^{2–}	C ₈	6–311G**	48	1176	150	692076	22500	–4.022595919	–4.022595919

TABLE VI.

Comparison of Calculation Results under Condition That Point Group is C_{nv} or C_{nh} (Energy Unit, au).

Model	G	Basis	Orbital	n_2	N_2	n_4	$N(g, d)$	SCF Energy	SOT-SCF Energy
H_3^+	C_{3v}	6-311G (<i>df, pd</i>)	33	561	114	157641	12996	-0.960351546	-0.960351546
H_3^-	C_{3v}	6-311G (<i>df, pd</i>)	33	561	114	157641	12996	-0.823959193	-0.823959193
H_4^{2+}	C_{4v}	6-311G**	24	300	53	45150	2809	-0.845979906	-0.845979906
H_4^{2-}	C_{4v}	6-311G**	24	300	53	45150	2809	-1.734286811	-1.734286811
H_{10}	C_{5v}	6-31G	20	210	26	22155	676	-5.370254684	-5.370254684
H_6	C_{6v}	6-311G**	36	666	74	222111	5476	-3.055434873	-3.055434873
H_4	C_{2h}	6-311G	12	78	24	3081	576	-1.841853161	-1.841853161
H_6	C_{3h}	6-311G	18	171	30	14706	900	-2.604501305	-2.604501304
H_8	C_{4h}	6-311G	24	300	42	45150	1764	-3.697641489	-3.697641489
H_{10}^{2+}	C_{5h}	6-311G	30	465	48	108345	2304	-3.915570966	-3.915570966
H_{10}^{2-}	C_{5h}	6-311G	30	465	48	108345	2304	-4.772172984	-4.772172985
H_{12}	C_{6h}	6-311G	36	666	60	222111	3600	-6.017923436	-6.017923436

- For the same system, SOT-SCF calculations were performed by making use of the molecular point group or its subgroups. For example, H_6 (C_6) and H_6 (C_{6v}) are the same system, but the SOs and integrals are classified according to different symmetric conditions (C_6 or C_{6v}). Apparently the higher the molecular symmetry is, the more efficient the calculation.
- The bond distances in the model systems are arbitrary and the total energies including SCF energies and SOT-SCF energies should not be overinterpreted. However, our data do suggest that the absolute differences between SCF energies and SOT-SCF energies are less than 10^{-8} and fall in the range of acceptable

calculation errors. The coincidence between the SCF and the SOT-SCF calculation results confirms the reliability of eq. (68).

- Regarding the geometric structures of the model systems, for single-axis groups most of the cases are planar (such as C_n and C_{nv}) and the others are of two layers (such as C_{nh} , D_{nd} , and S_n). For higher symmetric point groups, several typical structures like tetrahedron (T_d), octahedron (O_h), and icosahedron (I) are chosen.
- The models can be neutral or ionic. In the cases in which the density matrices in neutral systems are unable to satisfy the requirement of symmetry (in this case molecules have to deform to decrease their own symmetries),

TABLE VII.

Comparison of Calculation Results under Condition That Point Group is D_{nd} or S_n (Energy Unit, au).

Model	G	Basis	Orbital	n_2	N_2	n_4	$N(g, d)$	SCF Energy	SOT-SCF Energy
H_4^{2+}	D_{2d}	6-311G (<i>df, pd</i>)	44	990	142	490545	20164	-0.846258571	-0.846258575
H_4^{2-}	D_{2d}	6-311G (<i>df, pd</i>)	44	990	142	490545	20164	-1.734338736	-1.734338736
H_6	D_{3d}	6-311G**	36	666	68	222111	4624	-3.055434873	-3.055434873
H_6	D_{3d}	6-311G (<i>df, pd</i>)	66	2211	208	2445366	43264	-3.055929816	-3.055929816
H_8^{2+}	D_{4d}	6-311G**	48	1176	89	692076	7921	-3.287565678	-3.287565678
H_8^{2-}	D_{4d}	6-311G**	48	1176	89	692076	7921	-4.022595919	-4.022595919
H_{10}	D_{5d}	6-31G	20	210	18	27155	324	-5.370254684	-5.370254684
H_{12}^{2+}	D_{6d}	6-31G	24	300	21	45150	441	-5.438106101	-5.438106101
H_{12}^{2-}	D_{6d}	6-31G	24	300	21	45150	441	-5.650418106	-5.650418109
H_4	S_4	6-311G**	24	300	78	45150	6084	-1.821966657	-1.821966657
H_6^{2+}	S_6	6-311G**	36	666	114	222111	12996	-1.984318611	-1.984318611
H_6^{2-}	S_6	6-311G**	36	666	114	222111	12996	-2.693373410	-2.693373410
H_8	S_8	6-311G**	48	1176	150	692076	22500	-3.953526275	-3.953526275

TABLE VIII.
Comparison of Calculation Results under Condition That Point Group is D_n or D_{nh} (Energy Unit, au).

Model	G	Basis	Orbital	n_2	N_2	n_4	$N(g, d)$	SCF Energy	SOT-SCF Energy
H ₄	D_2	6-311G**	24	300	84	45150	7058	-1.844082520	-1.844082520
H ₆	D_3	6-311G**	36	666	120	222111	14400	-2.747877061	-2.747877061
H ₈	D_4	6-31G	16	136	22	9316	484	-3.673605157	-3.672605157
H ₁₀	D_5	6-31G	20	210	26	22155	676	-4.682848184	-4.682848184
H ₁₂	D_6	6-31G	24	300	32	45150	1024	-6.013368201	-6.013368201
H ₄	D_{2h}	6-311G**	24	300	64	45150	4096	-1.844082520	-1.844082520
H ₆	D_{3h}	6-311G**	36	666	74	222111	5476	-2.747877061	-2.747877061
H ₈	D_{4h}	6-311G**	48	1176	126	692076	11236	-4.022595919	-4.022595919
H ₁₀ ²⁺	D_{5h}	6-31G	20	210	18	22155	324	-3.930097527	-3.930097527
H ₁₀ ²⁻	D_{5h}	6-31G	20	210	18	22155	324	-4.022595919	-4.022595919
H ₁₂	D_{6h}	6-31G	24	300	24	45150	576	-6.013368201	-6.013368201
H ₈ ²⁺	D_{8h}	6-311G	48	1176	72	692076	5184	-3.287565678	-3.287565678

positively or negatively charged systems, whose density matrices are symmetric, are employed.

6. The most important data in these tables are n_4 and $N(g, d)$, whose ratio increases with the increasing of K_G . For the higher symmetric point groups $I(H_{12})$, $n_4/N(g, d) = 222,111/576 = 740$, $O_h(CH_6)$ $n_4/N(g, d) = 1,103,355/8464 = 130$, $T_d(CH_4)$ $n_4/N(g, d) = 406,156/7225 = 56$. For the lower symmetric point groups such as $C_{2v}(H_2O)$, $n_4/N(g, d) = 108,345/32,767 = 3.3$, and $C_{\infty v}(HF)$, $n_4/N(g, d) = 221,111/196,000 = 11.3$.

Conclusively, it is clear that for higher symmetric systems the SOT-SCF method is of higher calculation efficiency.

SOT-CI Approach

Let i and j be two occupied SOs and a and b be two virtual SOs. For any two-rank SOT $|ij\rangle$ there is a following relationship under G :

$$g|ij\rangle = \varepsilon|i'j'\rangle. \tag{70}$$

For a character 2-electron basis $|IJ\rangle$ (namely, a two-rank character tensor), the operation of the

TABLE IX.
Comparison of Calculation Results with Other Higher Point Groups (Energy Unit, au).

Model	G	Basis	Orbital	n_2	N_2	n_4	$N(g, d)$	SCF Energy	SOT-SCF Energy
CH ₄	T_d	6-311G**	42	903	85	408156	7225	-40.20880760	-40.20880760
CH ₆ ²⁺	O_h	6-311G**	54	1485	92	1103355	8464	-40.24181166	-40.24181166
CH ₆ ²⁻	O_h	6-311G**	54	1485	92	1103355	8464	-40.63775303	-40.63775303
H ₂ O	C_{2v}	6-311G**	30	465	181	108345	32761	-76.04406313	-76.04406313
C ₅ H ₅ ⁻	C_5	6-311G	55	1540	308	1186570	94864	-191.9451321	-191.9451321
CH ₁₀ ²⁺	D_{5d}	6-31G	29	435	44	94830	1936	-40.63951213	-40.63951213
HF	$C_{\infty v}$	6-311G (df, pd)	36	666	140	222111	19600	-100.0487973	-100.0487973
N ₂	$D_{\infty h}$	6-311G**	36	666	94	222111	8836	-108.9569172	-108.9569172
H ₆	T_h	6-311G**	36	666	50	222111	2500	-2.772349530	-2.772349529
H ₂	$D_{\infty h}$	6-311G (df, pd)	22	561	82	157641	1444	-1.133249814	-1.133249814
H ₄ ²⁺	T_d	6-311G**	24	300	27	45150	729	-.9343830815	-.9343830813
H ₄ ⁴⁻	T_d	6-311G**	32	300	27	45150	729	-.5120913696	-.5120913696
H ₁₂	I	6-311G	36	666	24	222111	576	-2.784885565	-2.784885564

projection operator $P^{[\lambda]}$ [see eq. (50)] will result in a 2-electron function of the irreducible representation λ :

$$F(IJ, \lambda) = P^{[\lambda]}|IJ\rangle. \quad (71)$$

$F(IJ, \lambda)$ seems very complicated, but in the practical sense the evaluation of the matrix elements between $F(IJ, \lambda)$ is rather straightforward according to eqs. (57) and (58) and we do not even need to know the complete form of $F(IJ, \lambda)$. Let a^+ be a creation operator, i^- be an annihilation operator, and $|0\rangle$ be a vacuum state. It is known that $|ab\rangle = a^+b^+|0\rangle$ and $j^-i^-|ij\rangle = |0\rangle$. The symmetric creation operator and the symmetric annihilation operator are

$$P(A^+B^+, \lambda) = P^{[\lambda]}A^+B^+ \quad (72)$$

and

$$P(J^-I^-, \lambda) = P^{[\lambda]}J^-I^-, \quad (73)$$

respectively. The symmetric creation-annihilation operator is

$$P(A^+B^+, J^-I^-, \lambda) = P(A^+B^+, \lambda)P(J^-I^-, \lambda), \quad (74)$$

which describes an excitation of a couple of electrons from the occupied space $\{ij\}$ of the specific symmetry to the virtual space $\{ab\}$ of the same symmetry. If Φ_0 is the ground state wave function resulting from the SCF calculations, $P(A^+B^+, J^-I^-, \lambda)\Phi_0 = \Phi(AB, IJ, \lambda)$ represents a double-electron excited state. According to the Brillouin theorem, single-electron excited states have no first-order contribution to the SCF wave function; thus, for the time being we consider the double-electron excited configurations only. The SOT-double configuration iteration (DCI) wave function is

$$\Psi = \Phi_0 + \sum_{\lambda, IJ, AB} \Phi(AB, IJ, \lambda)c(AB, IJ, \lambda), \quad (75)$$

where $c(AB, IJ, \lambda)$ is the coefficient of $\Phi(AB, IJ, \lambda)$, which is a combination of the SOT-Slater configurations of the specific symmetry λ . The SOT-DCI wave function has the following properties:

1. $\Phi(AB, IJ, \lambda)$ is of the same symmetry as Φ_0 .
2. $g\Phi(AB, IJ, \lambda)^*\Phi(AB, IJ, \lambda) = \Phi(AB, IJ, \lambda)^*\Phi(AB, IJ, \lambda)$ and $g\Psi^*\Psi = \Psi^*\Psi$. In other words, density function belongs to the totally symmetric irreducible representation.
3. Because the SOT-DCI wave function Ψ includes all possible double-excited configura-

tions, it is equivalent to the traditional DCI wave function;

4. Based on the traditional DCI theory, if the numbers of occupied MOs and virtual MOs are n_1 and n_2 , respectively, in total there are $n_1(2) = n_1(n_1 + 1)/2$ 2-electron occupied SOTs and $n_2(2) = n_2(n_2 + 1)/2$ 2-electron virtual SOTs. Consequently, there are $n(\text{DCI}) = n_1(2)n_2(2)$ DCI configurations. Because the ratio between the number of all possible 2-electron SOTs and the number of character 2-electron SOTs is about K_G , there is

$$\frac{n(\text{DCI})}{n(\text{SOT} - \text{DCI})} \propto \frac{K_G K_G}{n(\lambda)}, \quad (76)$$

where $n(\lambda) = \sum_{\lambda} d_{\lambda}$.

5. Regarding the Hamiltonian matrix element between $\Phi(AB, IJ, \lambda)$ and $\Phi(A'B', I'J', \lambda')$, if $\lambda \neq \lambda'$ or $\delta_{AA'} + \delta_{BB'} + \delta_{II'} + \delta_{JJ'} < 2$, the matrix element is equal to zero. Thus, the number of nonzero matrix elements is very small. A nonzero matrix element is related to the parts not in common between two configuration functions and can be evaluated easily with eq. (57) introduced in the pretext.
6. According to the algorithm in the direct CI method, there is

$$c_i = \sum_j \frac{H_{ij}c_j}{E_i - E}. \quad (77)$$

Similarly in the SOT-DCI approach, the iteration formula is

$$c(AB, IJ, \lambda) = \sum_{A'B', I'J'} \frac{H(A'B', I'J'; AB, IJ, \lambda) \times c(A'B', I'J', \lambda)}{E(AB, IJ, \lambda) - E}. \quad (78)$$

Because the number of nonzero $H(A'B', I'J'; AB, IJ, \lambda)$ in eq. (78) is far fewer than the number of nonzero H_{ij} in eq. (77), the number of multiplication operations to derive a configuration's coefficient (AB, IJ, λ) in the SOT-DCI approach is much fewer than C_i in the traditional DCI method. Furthermore, according to eq. (76), the ratio of the numbers of C_i and $C(AB, IJ, \lambda)$ is approximately equal to $K_G K_G / n(\lambda)$. As a consequence, the SOT-DCI should be at least K_G^2 times more efficient than the traditional DCI method. This principle is also applicable to any other post-SCF calculations.

Discussion

In this article we developed the SOT method, whose key is the definition of SOs. Under the molecular point groups, an SO can be transformed to another equivalent SO or simply itself. This virtue is preserved for SOTs, too, which are the products of SOs. Based upon the scheme using a local coordinate system for ligand atoms and a standard coordinate system for the central atom, a general scheme to construct SOs is proposed. The SO basis functions $\{M\}$ are standardized according to the irreducible representations of subgroups of molecular point group G for all molecules. Normally these SOs are localized AOs. SOs and SOTs are transformed according to the given SOT representations and an SOT can be specified by $M(s, t, u)$. SOTs with the same s and u but different t can permute but do not mix with one another under G . Thus, a CT $M(s, 1, u)$ is defined for the series $\{M(s, t, u), t = 1, 2, \dots, K_s\}$. In the evaluation of the matrix element of a tensor $M(N)$, only $M(s, 1, u)$ that satisfies the nonzero condition eq. (44) is a physical factor. The complete set of SOTs forms an SOT group, and there is a one to one correspondence between a point group G and an SOT group. The SOT method realizes the complete separation of physical factors and geometric factors and is equivalent to the traditional irreducible representation tensor method. However, in the latter method for point groups with degenerate irreducible representations, a matrix element may be a mixture of several terms and there is a so-called k^N problem, which will make calculations very time consuming as N increases. In our method, on the other hand, the matrix element of SOT is only a single term for any N . Moreover, coupling coefficients are necessary to evaluate matrix elements in the irreducible representation tensor method and different sets of coupling coefficients are needed for different point groups. The SOT method uses a general and closed arithmetic, and each SOT and each N th-rank tensor can be reduced to the product of a physical factor and a geometric factor and coupling coefficients are not involved.

It is known that the introduction of the ladder operators for the angular momentum and the spin-angular momentum, as well as the commutation relations among these operators in the $SO(3)$ rotation group, standardizes the group theory method for the many-electron atoms. Our work established a map between point group operators

and angular momentum operators. The eigenoperator g_a of SOT [see eq. (42)] corresponds to the angular momentum operators L^2 and L_z (as well as L_x and L_y), while the translation operator g_t [see eq. (43)] corresponds to the raising operator L^+ and the lowering operator L^- . Therefore, based on our SOT theory, the point group method in many-electron molecules will be standardized and the operations of point group symmetry are completely characterized by quantum numbers.

The present quantum chemistry software programs still have difficulties in making full use of point group symmetries due to the k^N problem. The SOT method can effectively exploit molecular symmetries prominently for higher symmetric systems and reduce the computation efforts by $k^N \rightarrow 1^N \rightarrow 1$. To test the SOT theory we wrote a preliminary SOT-SCF program that can construct SOs, SOT(2)s, and SOT(4)s and can completely separate the physical factors and geometric factors from 1-electron and 2-electron integrals. Because molecular integrals are the foundation for all *ab initio* calculations, our SOT method screens the redundant variables resulting from the introduction of symmetries of point groups and consequently raises the calculation efficiency in the SCF method. By applying the SOT method to the SCF calculations, we proposed a crucial equation [eq. (68)] that can simplify the multiplication manipulations in the SCF iterations. While the traditional SCF calculations adopt eq. (60), the ratio between the numbers of multiplication operations by using eq. (60) and by eq. (68) is $n_4/N(g, d)$. The higher the molecular symmetry is, the higher the order of the molecular point group and, subsequently, the higher the $n_4/N(g, d)$. With the increase of the number of MOs in systems, the latter approaches $(K_G)^2$. Thus, compared to the traditional SCF method, the CPU time and the disk and memory requirement in the SOT-SCF method decrease in the order of the square of the order of a point group. It is worthwhile to point out that the use of the symmetries of point groups is only one of several means to simplify the SCF calculations for symmetric molecules. There are other possible means as well. When the basis sets are Gauss functions, for large molecules there are a large number of 2-electron integrals close to zero and that can be discarded; as a result, the practical computation scales as $n^{2.7}$. Recently, Schwegler and Challacombe¹⁸ developed a hierarchical multipole method that leads to a linear scaling algorithm for calculation of the Fock matrix. However, no matter whether the computation scales as n^4 ,

$n^{2.7}$, or n , the SOT-SCF method can reduce the computation efforts further by $(K_G)^2$.

The precondition for the use of eq. (68) is that in the SCF iterations the density matrices are of the same symmetries as the molecular frames. In other words, the density matrices must belong to the totally symmetric representation.

Although in the present article we only performed calculations on closed-shell systems, the method can also be applied to open-shell and post-SCF calculations. In the meanwhile, the SOT method may also be applied to the areas of semiempirical and density functional theory approaches. For the higher symmetric and the larger molecules, the SOT method has higher computation efficiencies.

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